IV REUNIÓN NACIONAL DE DIOXINAS, FURANOS Y COMPUESTOS ORGÁNICOS PERSISTENTES RELACIONADOS

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APPLICATION OF MS·3 SYSTEMS FOR EVALUATING THE TRANSFER OF EMERGING POLLUTANTS FROM AMENDED AGRICULTURAL SOILS TO EARTHWORMS

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Introduction
The socio-economic changes happening for recent decades, the development of the industry in different sectors, the exorbitant increase in human population, and its highly consuming practices, have resulted in a significant increase in organic waste production that could generate environmental problems. Part of this organic pollution ends up in wastewater and in the municipal solid waste (MSW). Although most pollutants do not necessarily cause a threat to the environment because their low concentration and/or availability to be metabolized by microorganisms, there are some organic compounds, such as flame retardants including: polybrominated diphenyl ethers (PBDEs),¹ decabromodiphenylethane (DBDPE),²,³ dechloranes (Dec 602, 603, 604 and 605),⁴,⁵ and also some perfluorinated compounds (PFCs),⁶,⁷ among others, that do not break down easily during wastewater treatment and/or MSW composting. Thus, presence of these chemicals in sludge and/or MSW compost can originate problems due to their toxicity, bioaccumulation, and transfer through the food chain, when these wastes are used for agricultural purposes. Consequently, although this kind of wastes represents an inexpensive nutrient source and soil conditioner, their use for agricultural production requires that environmental risks be also documented. Considering this, the present study was designed to evaluate the bioaccumulation of PBDEs, DBDPE, DP, Dec 602, Dec 603, Dec 604, CP, mirex, and perfluorinated alkyl substances in earthworms exposed to an agricultural soil amended with four organic wastes: two sewage sludge, and two MSW composts.

Earthworms consume large amounts of soil and their thin cuticle is in almost constant contact with soil. If an organic contaminant is bioavailable and bioaccumulate in earthworms, it will enter the terrestrial food chain, as earthworms are eaten by many organisms from higher trophic levels. Therefore, earthworms have become common model organisms for testing toxicity and bioavailability of contaminants in soil, especially for organic compounds. Several studies have shown that various organic compounds are bioaccumulated in earthworms.⁸

Materials and methods
Multi species soil systems (MS·3)
These systems (MS-3) were used as rapid tests for assessing the presence of PBDEs (21 congeners from tri to decaBDE), DBDPE, DP, Dec 602, Dec 603, Dec 604, CP, mirex, and perfluorinated alkyl substances (4 sulphonates, 13 carboxilic acids, and 3 sulphonamides), both in waste-soil mixtures and in the exposed earthworms. MS-3 is a terrestrial microcosm that has already been used with the antibiotic doxycycline in aged spiked pig manure⁹ or sewage sludge amended soil.¹⁰ In the present study, PVC cylinders (20 cm internal diameter and 30 cm high) covered by a fine nylon mesh at the bottom to avoid soil loss were used. The leachates were collected in a glass bottle by means of a funnel in each MS-3. The columns were installed in a climate room with a light–dark cycle of 16–8 h, air condition of 21±1ºC, and humidity of 55–60%. The MS-3 columns were saturated with spring water; after that 30 plant seeds (Triticum aestivum, Brassica rapa and Vicia sativa), and 20 earthworms (Eisenia fetida) were introduced. During the exposure period (21 days) the MS-3 columns were daily irrigated (100 ml/day) to simulate 1000 mm rainfall/year.

The soil used in this study was a typical agricultural soil with known history; pesticides and fertilizers had not been applied at least for the last 10 years. The soil sample was taken within the top 20 cm soil layer, sieved (2 mm mesh), and homogenized before use. Four MS-3 experiments were performed using different organic wastes: an aerobically digested MSW compost (W1), an anaerobically digested thermal drying sludge (W2), an aerobically digested composted sewage sludge (W3), and an anaerobically digested MSW compost (W4). Wastes
application rates were calculated by considering the N requirement of plants and were added to control the soil used to fill the microcosm columns.

Waste samples were kindly provided by Spanish waste management companies and wastewater treatment plants. Each MS-3 was filled with 8 kg of the waste-amended soil (120 - 555 g of waste in each treatment). The four treatments and the control were performed in triplicate, although due to small sample size (especially for earthworms) chemical analyses were conducted with pooled samples.

**Extraction, purification and analytical analysis**

Complete details of analytical procedures have been described elsewhere. Procedural blanks were processed and analyzed under the same conditions. Concentrations obtained were used to correct those for the samples analysed. In this way, the final result of each sample is obtained by subtracting the blank values.

**Results and discussion**

Concentrations of PBDEs (from tri to decaBDE), DBDPE, DP (sum of anti- and syn-DP), Dec 602, Dec 603, perfluorinated alkyl sulphonates (PFSAs), and perfluorinated carboxylic acids (PFCAs) are reported in Figure 1 for the wastes, amended soils, and earthworms studied in the four treatments. Data for laboratory bred earthworms and control soil are also included.

The four wastes considered in this study presented a similar FR pattern being PBDEs the predominant chemicals following in decreasing order by DBDPE and DP (~ ng/g d.w.). Concentrations of Dec 603, Dec 602, and CP (~ pg/g d.w.) were also quantified but at one order of magnitude lower than DP. However Mirex levels were below method detection limits (MDLs) in all cases. A similar PBDEs pattern was obtained both in sewage sludge and MSW compost wastes, being BDE-209 the major congener (accounting 78 ± 4% to the total PBDEs; mean ± SD), following in decreasing order by BDE-207 (5 ± 1%), BDE-206 (6 ± 3%), BDE-99 (4 ± 1%), BDE-47 (2 ± 1%), and BDE-100, 183, 196, and 197 (≤ 1%). This result proves the use of DecaBDE commercial mixtures in Spain. The four wastes also presented a similar dechlorane pattern (DP >> Dec 603 > Dec 062), which is in agreement to the one previously reported in Spanish sewage sludge.

Concentrations of perfluoro alkyl substances are in the same order of magnitude than major FR (PBDEs, DBDPE and DP, ng/g d.w.). PFOS was the compound with higher concentrations, followed by PFDA and PFOA. Besides, PFC content in MSW compost (W1 and W4) is lower than that obtained in sewage sludge (W2 and W3).

As mentioned before, the amount of waste added to the soil was determined by considering the agronomic requirement of the plants grown in the MS-3. Therefore, relative low amounts of waste (120 - 555 g) were added. Concentrations in the waste amended soils are low; however presence of all these organic pollutants evidences their transfer during waste application and allows bioaccumulation studies. Chemical pattern in the waste amended soil (see Figure 1) reflect the one obtained in the wastes. Nevertheless, FR pollutant pattern varies when it comes to earthworms, where PBDEs, DP, Dec 602 and Dec 603 were quantified, but levels of DBDPE and CP were below MDLs. Consequently, it can be inferred that these chemicals present important differences in terms of bioaccumulation.

Considering PBDEs, an enrichment in lower brominated congeners (BDE-47 (7 ± 2%), BDE-99 (7 ± 1%), and BDE-100 (2 ± 1%)) in earthworms compare to amended soils could be observed. Bioaccumulation differences could be also distinguished when BDE-209 and DBDPE levels are compared. Both compounds were quantified at relative high levels in amended soils (up to 19 ng/g d.w.), however BDE-209 was only observed in earthworms, suggesting higher bioaccumulation rates for BDE-209 in comparison to those for its proposed substitute. Similar behaviour takes place with Dec 602 and 603. While levels of Dec 603 in the amended soil are higher than those found for Dec 602, bioaccumulation of the former appears to be lower than the latter.

PFC levels in earthworms are also higher than those related to waste amended soils, indicating bioaccumulation has taken place. In this case, results suggest higher bioaccumulation rates for longer chain perflourinated carboxylic acids.

To the best of our knowledge, this is the first time DP, Dec 602 and 603 have been detected in earthworms (*Eisenia fetida*). Data obtained in this study demonstrate that MS-3 system is a reliable tool for testing organic pollutant transfer from waste amended soils to terrestrial organisms.
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References
Figure 1. Concentrations of ∑PBDEs, DBDPE, ∑DP, Dec 602, Dec 603, CP, ∑PFSAs, ∑PFCAs, in the wastes (red), soils (green), and earthworms (orange).